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(54) [Title of the Invention]

OLEFIN TYPE COPOLYMER RUBBER COMPOSITION

(57) [Abstract]

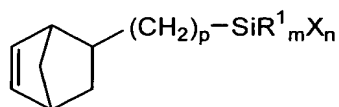
[Constitution] A silyl group-containing olefin type copolymer obtained by copolymerizing a silyl group-containing monomer with an olefin type monomer and a non-conjugated diene in the presence of a Ziegler-Natta catalyst is allowed to react with specified alcohol and alkoxide to obtain a copolymer and, then, the thus-obtained copolymer is blended with a silica type filler and titanium oxide at respective specified rates, to thereby obtain an olefin type copolymer rubber composition.

[Effect] Not only having an excellent tensile property but also being excellent in a coloring property compared with a conventional composition.

[Claims]

[Claim 1] An olefin type copolymer rubber composition, wherein (A) 100 parts by weight of a rubber component containing at least 20% by weight of a silyl group-containing olefin type copolymer, in which a content of a bonded silyl group-containing unsaturated compound is 0.5 to 5.0% by weight, which is obtained by firstly copolymerizing (a) at least two types of olefin type monomers, (b) a non-conjugated diene and (c) a silyl group-containing unsaturated compound represented by the following general formula:

[Chemical 1]



(I)

and/or



(II)

wherein  $\text{R}^1$  represents a hydrocarbon group having 1 to 20 carbon atoms;

X represents any one halogen of chlorine, bromine and iodine;

p represents an integer of 0 to 5;

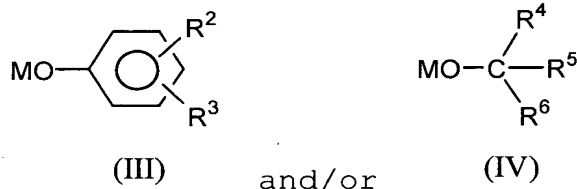
q represents an integer of 1 to 20;

m represents an integer of 0 to 2; and

n represents an integer of 1 to 3, wherein a relation of  $m+n=3$  is established,

in the presence of a catalyst comprising a transition metal compound and an organometallic compound and, then, by allowing the resultant copolymer to react with a compound represented by the following general formula:

[Chemical 2]



wherein M represents a hydrogen atom or any one alkaline metal of lithium, sodium and potassium;

$\text{R}^2$ ,  $\text{R}^3$ ,  $\text{R}^4$ ,  $\text{R}^5$  and  $\text{R}^6$  each represent the same as the above-described  $\text{R}^1$  or any one of a hydrogen atom, a hydrocarbon group having 1 to 20 carbon atoms and containing a tertiary amino group and a tertiary amino group, wherein entire carbon atoms of  $\text{R}^4$ ,  $\text{R}^5$  and  $\text{R}^6$  are 3 or more,

is blended with (B) 20 to 150 parts by weight of a silica type filler having a specific surface area of 160 to 350  $\text{m}^2/\text{g}$  and (C) 0 to 50 parts by weight of titanium oxide.

[Detailed Description of the Invention]

[0001]

[Industrial Applicability]

The present invention relates to an olefin type copolymer rubber composition which is excellent in a tensile property and a coloring property and blended with a silica type filler and titanium oxide.

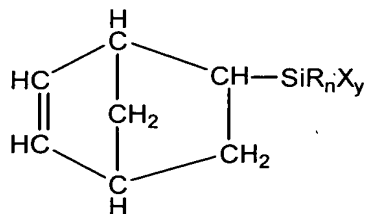
[0002]

[Prior Art]

Heretofore, in an olefin type copolymer rubber composition which is blended with a silica type filler, in order to obtain an excellent tensile property, an olefin type copolymer rubber into which a silyl group which has a reactivity with the silica type filler has been introduced has been used. As for a method for producing the olefin type copolymer rubber

into which the silyl group has been introduced, using a halosilane as represented by the following general formula:

[Chemical 3]



wherein R represents hydrogen or a C<sub>1</sub> to C<sub>6</sub> organic group;

X represents a halogen;

n represents an integer of 0 to 2; and

y represents an integer of 1 to 3, wherein n+y are equal to 3, as a copolymer component is described in JP-B-44-22501.

Further, a production method in which an ethylene type unsaturated organosilane as represented by the general formula: R<sub>n</sub>SiX<sub>4-n</sub>, wherein X represents a highly hydrolysable group except an oxygen-containing group; n represents an integer of 1 to 3; and R represents a group selected from the group consisting of hydrogen, substituted or unsubstituted cyclic or heterocyclic alkyl, aryl, alkylaryl and arylalkyl group, wherein at least one R group has an unsaturated carbon-carbon bond is used as a copolymer component is described in JP-B-58-38443.

Further, at the time of subjecting the olefin type copolymer rubber blended with the silica type filler to coloring, when a coloring pigment is directly added, since transparency of the olefin type copolymer rubber blended with the silica type filler is high, coloring deficiency is generated. Therefore, in order to prevent the coloring deficiency, it has been known to further add titanium oxide

which is a white pigment.

[0003]

[Problems that the Invention is to Solve]

However, in a silyl group-containing olefin type copolymer produced by a prior art, since the silyl group thereof has a highly hydrolyzable property, the copolymer reacts with moisture in the air and is hydrolyzed, to thereby produce a silanol which is, then, easily dehydrate-condensed. For this reason, the copolymer loses a portion which reacts with the silica type filler and, therefore, improvement of tensile property of the copolymer can not be noticed.

In order to prevent such generation of the silanol as described above, it has been tried that a functional group having a hydrolysable property in the silyl group was allowed to react with a lower alcohol, an amine or a carboxylic acid. However, under conditions of producing a copolymer, since a bond generated by the reaction is unstable, a stable copolymer can not be produced.

Further, in order to solve this problem, when a stable bond is introduced thereto at the time of production, since a bond is not formed between the silyl group and the silica type filler at the time of blend-kneading the silica type filler, an improvement of the tensile property can not be noticed.

On the other hand, when the olefin type copolymer rubber composition blended with the silica type filler is added with titanium oxide at the time of coloring, it is noticed that, although a coloring property is enhanced, the tensile property is deteriorated.

[0004]

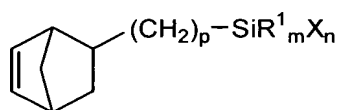
[Means for Solving the Problems]

The present inventors have exerted intensive studies for solving these problems and, as a result, have found that a copolymer produced by allowing an olefin type copolymer prepared by copolymerizing a silyl group-containing unsaturated compound represented by the general formula of Chemical 4 to react with an alcohol or an alkoxide represented by the general formula of Chemical 5 is stable at the time of production and exhibits an excellent tensile property when being blended with a silica type filler. Further, the present inventors have also found that, when the copolymer is used, decrease of the tensile property is small even at the time of being blended with titanium oxide, to thereby achieve the present invention.

[0005]

Namely, the present invention provides an olefin type copolymer rubber composition, wherein 100 parts by weight of a rubber component containing at least 20% by weight of a silyl group-containing olefin type copolymer, in which a content of a bonded silyl group-containing unsaturated compound is 0.5 to 5.0% by weight, which is obtained by firstly copolymerizing at least two types of olefin type monomers, a non-conjugated diene and a silyl group-containing unsaturated compound represented by the following general formula:

[Chemical 4]



(I)

and/or



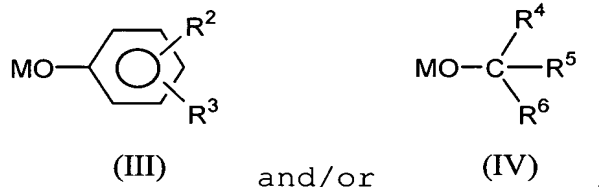
(II)

wherein  $\text{R}^1$  represents a hydrocarbon group having 1 to 20 carbon atoms; X represents any one halogen of chlorine,

bromine and iodine; p represents an integer of 0 to 5; q represents an integer of 1 to 20; m represents an integer of 0 to 2; and n represents an integer of 1 to 3, wherein a relation of  $m+n=3$  is established,

in the presence of a catalyst comprising a transition metal compound and an organometallic compound and, then, by allowing the resultant copolymer to react with a compound represented by the following general formula:

[Chemical 5]



wherein M represents a hydrogen atom or any one alkaline metal of lithium, sodium and potassium;  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  each represent the same as the above-described  $R^1$  or any one of a hydrogen atom, a hydrocarbon group having 1 to 20 carbon atoms and containing a tertiary amino group and a tertiary amino group, wherein entire carbon atoms of  $R^4$ ,  $R^5$  and  $R^6$  are 3 or more

is blended with 20 to 150 parts by weight of a silica type filler having a specific surface area of 160 to 350  $m^2/g$  and 0 to 50 parts by weight of titanium oxide.

[0006]

Hereinafter, the present invention is described in more detail. The silyl group-containing olefin type copolymer to be used in the invention can be used in a rubber component either individually or in combination of other rubber. However, it is necessary to contain the silyl group-containing olefin type

copolymer in an amount of 20% by weight or more. If the amount is less than 20% by weight, an improvement effect of silica enforcement can not be recognized.

[0007]

Further, the silica type filler to be blended in the rubber component containing the silyl group-containing ethylene type copolymer in the invention has a specific surface area of 160 to 350 m<sup>2</sup>/g and, preferably, 200 to 300 m<sup>2</sup>/g. When the specific surface area is less than 160 m<sup>2</sup>/g, a reaction efficiency with the silyl group is deteriorated and an effect of improvement of the tensile strength is small. When the specific surface area is more than 350 m<sup>2</sup>/g, a pore diameter of the silica type filler becomes small and a reactivity thereof with the silyl group is deteriorated, which is not favorable. As for the silica type filler, specifically, Nipsil VN<sub>3</sub> (trade name; manufactured by Nippon Silica Industrial Co., Ltd.), Carplex #67 (manufactured by Shionogi & Co., Ltd.) and Siltan A (manufactured by Mizusawa Chemical Co., Ltd.) are mentioned.

An amount of the silica type filler to be blended is, based on 100 parts by weight of rubber component, 20 to 150 parts by weight and, preferably, 30 to 70 parts by weight. When the amount of the silica type filler to be blended is less than 20 parts by weight, improvement of physical property is small, while, when it is more than 150 parts by weight, processability is deteriorated, which is not favorable.

An amount of titanium oxide to be used in the invention is, based on 100 parts by weight of the rubber component, 0 to 50 parts by weight and, preferably, 5 to 20 parts by weight. When it is more than 50 parts by weight, processability is deteriorated, which is not favorable.



[0008]

The catalyst to be used in manufacturing the olefin type copolymer in the invention is a Ziegler-Natta catalyst containing a transition metal compound and an organometallic compound. As for such transition metal compounds, halogenated compounds of Ti, Zr, V and Cr can be used and, particularly, a Ti or V compound is preferred. As for such organometallic compounds, alkyl compounds of, for example, Al, Mg and Li or haloalkyl compounds thereof are preferred.

[0009]

Further, a halogenated acetic acid ester such as trichloroacetic acid ethyl, trichloroacetic acid butyl or dichloroacetic acid; a halogen-substituted butenoic acid ester such as 1,1,2,3,3-pentachlorobutenoic acid butyl or 1,1,2,3-tetrachlorobutenoic acid ethyl; and a halogen-containing organic compound such as  $\alpha,\alpha,\alpha$ -trichlorotoluene or hexachlorobutadiene can be added as a polymerization activity improving agent.

As for such olefin type monomers to be used in the invention, ethylene, propylene, butene-1, pentene-1, hexene-1, heptene-1, octene-1, nonene-1, decene-1, 4-methyl pentene-1, 4-methyl hexene-1, 4,4-dimethyl pentene-1, 5-methyl heptene-1, 6-methyl heptene-1 and the like are mentioned and, it is preferable to use ethylene and propylene in combination or ethylene and butene-1 in combination. A preferable composition ratio of ethylene and propylene is 20 to 80 mol of ethylene against 80 to 20 mol of propylene. Further, a preferable composition ratio of ethylene and butene-1 is 90 to 50 mol of ethylene against 10 to 50 mol of butene-1.

On the other hand, as for such non-conjugated dienes to

be used in the invention, ethylidene norbornene, propenyl norbornene, dicyclopentadiene, 1,4-hexadiene and 4,7,8,9-tetrahydroindene and the like are mentioned.

[0010]

Next, examples of silyl group-containing unsaturated monomers as represented by the general formula of Chemical 4 to be used in the invention include 5-trichlorosilyl-2-norbornene, 5-methyl dichlorosilyl-2-norbornene, 5-dimethyl chlorosilyl-2-norbornene, 2-(5-norbornenyl)ethyl methyl dichlorosilane, 2-(5-norbornenyl)ethyl dimethyl chlorosilane, 2-(5-norbornenyl)propyl methyl dichlorosilane, 2-(5-norbornenyl)propyl dimethyl chlorosilane, 2-(5-norbornenyl)butyl methyl dichlorosilane, 2-(5-norbornenyl)butyl dimethyl chlorosilane, (2-propenyl)dimethyl chlorosilane, (2-propenyl)methyl dichlorosilane, (3-butenyl)dimethyl chlorosilane, (3-butenyl)methyl dichlorosilane, (3-butenyl)trichlorosilane, (4-pentenyl)dimethyl chlorosilane, (4-pentenyl)methyl dichlorosilane, (4-pentenyl)trichlorosilane, (5-hexenyl)dimethyl chlorosilane, (5-hexenyl) methyl dichlorosilane, (5-hexenyl)trichlorosilane, (6-heptenyl)dimethyl chlorosilane, (6-heptenyl) methyl dichlorosilane, (6-heptenyl)trichlorosilane, (7-octenyl)dimethyl chlorosilane, (7-octenyl)methyl dichlorosilane and (7-octenyl) trichlorosilane. As for compounds represented by the general formula of Chemical 4, (5-hexenyl)dimethyl chlorosilane, (7-octenyl)dimethyl chlorosilane, 5-methyl dichlorosilyl-2-norbornene, 5-dimethyl

chlorosilyl-2-norbornene, and 2-(5-norbornenyl)ethyl dimethyl chlorosilane are particularly preferred thereamong. [0011]

Examples of alcohols as represented by the general formula of Chemical 5 to be used in the invention include phenol, o-cresol, m-cresol, p-cresol, o-ethyl phenol, m-ethyl phenol, p-ethyl phenol, 3-dimethylamino phenol, 4-diethylamino phenol, 3-diethylamino phenol, 4-diethylamino phenol, 3-dimethylamino methyl phenol, 3-diethylamino methyl phenol, 2-methyl-2-propanol, 2-methyl-2-butanol, 2-methyl-2-pentanol, 6-diethylamino-2-hexanol, 6-dimethylamino-2-hexanol, 5-diethylamino-2-pentanol and 5-dimethylamino-2-pentanol. Examples of alkoxides as represented by the general formula of Chemical 5 includes lithium, sodium and potassium salts of the above-described alcohols.

[0012]

Polymerization solvents to be used in the invention are not particularly limited and examples thereof include n-pentane, n-hexane, cyclohexane, toluene and n-heptane and, thereamong, n-hexane is particularly preferred.

As for polymerization conditions, a temperature of -30 to 100°C and, preferably, 0 to 90°C and a pressure of 0 to 20 atoms and, preferably, 0 to 10 atoms are mentioned. Next, at the time a reaction ratio is sufficiently elevated, the compound as represented by the general formula of Chemical 5 is excessively added to not only terminate a polymerization reaction but also to allow to react with the silyl group introduced in the copolymer. In order to promote the reaction, a base such as triethyl amine or pyridine may be used. In a

case in which the compound as represented by the general formula of Chemical 5 does not react with all of the silyl groups, in order to prevent cross-linking, a highly reactive lower alcohol such as methanol or ethanol can also be added. Subsequently, the silyl group-containing olefin type copolymer can be obtained by removing unreacted monomer and solvent.

[0013]

A content of the non-conjugated diene in the thus-obtained silyl group-containing olefin type copolymer is 50 or less and, preferably, 5 to 40 in terms of an iodine value. When the iodine value is more than 50, ozone resistance is deteriorated, which is not favorable.

Further, a content of the silyl group-containing unsaturated compound as represented by the general formula of Chemical 6 or 7 in the silyl group-containing olefin polymers is 0.5 to 5.0% by weight and, preferably, 1.0 to 3.0% by weight. When the content thereof is less than 0.5% by weight, an effect of improvement of the physical property is small, while, when the content thereof is more than 5.0% by weight, the reaction with the silica type filler is unduly progressed and, then, the rubber property intrinsic to the copolymer is lost, which is not favorable.

A Mooney viscosity ( $ML_{1+4}$ , 100°C) of the silyl group-containing olefin type copolymer is in the range of preferably from 10 to 200 and, more preferably, 20 to 100. When the Mooney viscosity is less than 10, the tensile property is deteriorated, which is not favorable, while, when the Mooney viscosity is more than 200, the processability is deteriorated, which is not favorable, either.

As for other rubbers capable of being blended to the silyl

group-containing olefin type copolymer, an ethylene-propylene rubber, a styrene-butadiene rubber, a butadiene rubber and a natural rubber are mentioned and, particularly, the ethylene-propylene rubber is preferred.

[0014]

The copolymer rubber composition according to the invention can optionally be blended with an oil extending agent such as a paraffin process oil, various types of other additives and vulcanizing agents and, then, used. Further, a filler such as carbon black or the like can be mixed to the silica type filler and, then, used. The copolymer rubber composition according to the invention can be utilized in various fields such as exterior articles for automobiles, rubber hoses, rubber sheets and vibration damping rubber by making use of excellent properties thereof.

[0015]

[Examples]

Hereinafter, the present invention is described in more detail with reference to embodiments but is not limited thereto within the scope of the invention. Further, various measurements in embodiments are based on the following: a propylene content, a 1-butene content and an iodine value are each determined by an infra-red method in accordance with a pre-calculated analytical curve; and a content of silyl group-containing monomer is determined by an infra-red method in accordance with a previously constructed analytical curve based on an absorption of  $\text{-Si-CH}_3$  to be observed in the vicinity of  $1260\text{ cm}^{-1}$  in an infra-red spectrum. A fact that diethylamino phenoxy silane or phenoxysilane has been generated by a reaction between the silyl group and 3-diethylamino phenol or

phenol was confirmed by observing a UV peak based on a phenoxy group by means of a GPU-UV method. A Mooney viscosity was measured under conditions that preheating: one minute; measuring time: four minutes; and temperature: 100°C. A tensile property was measured in accordance with JIS K 6301. A degree of whiteness was measured by using a Hunter colorimetric photometer.

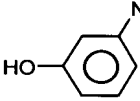
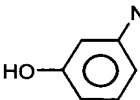
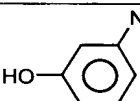
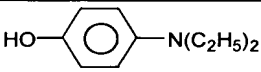
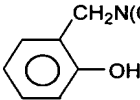
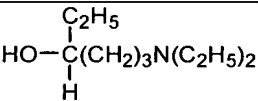
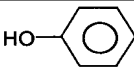
[0016]

[Preparation Example 1]

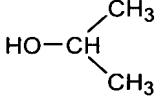
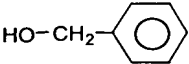
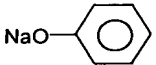
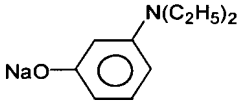
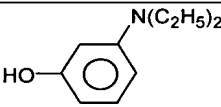
3 liter of purified n-hexane was filled in a separable flask of 5-liter capacity which has previously been substituted with an N<sub>2</sub> gas and, then, a mixed gas of ethylene, propylene and hydrogen with a mixing ratio of 7:8:2 (in mol ratio) was dissolved therein at room temperature in advance. Next, 2-(5-norbornenyl)ethyl dimethyl chlorosilane was added thereto in an amount in each of Tables 1 and 2. Further, 9.0 mmol of ethyl aluminum sesquichloride (AlEt<sub>1.5</sub>Cl<sub>1.5</sub>) was added thereto. Subsequently, 0.9 mmol of VOCl<sub>3</sub> was loaded in the flask while 6.0 ml of ethylidene norbornene was gradually added by using a feed pump, to thereby initiate a polymerization reaction. The polymerization reaction was continuously performed at 20°C while a mixed gas of ethylene, propylene and hydrogen was fed in a vapor phase and stirred during the polymerization reaction. After 30 minutes have elapsed, compounds as represented by the general formula of Chemical 5 as shown in Tables 1 and 2 were added. After 10 minutes have elapsed, triethyl amine was added thereto in an amount as shown in each of Tables 1 and 2 and, then, further stirred for 20 minutes. Next, 10 ml of dehydrated methanol was added thereto. The resultant copolymer solution was added with a large amount

of methanol to be agglomerated. The resultant copolymer was dried by using a hot roll.

[Table 1]

Polymer	Addition amount of silyl group-containing compound (mmol)	Compound as represented by general formula of Chemical 5 and addition amount thereof (mmol)	Addition amount of triethyl amine (mmol)
A	9.0	 (45)	45
B	4.0	 (38)	38
C	18.0	 (53)	53
D	9.0	 (45)	45
E	9.0	 (45)	45
F	9.0	 (45)	45
G	9.0	 (45)	45

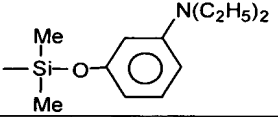
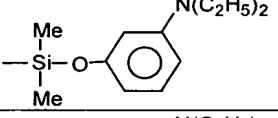
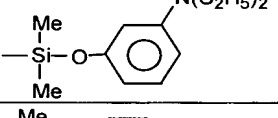
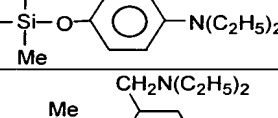
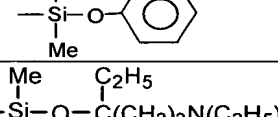
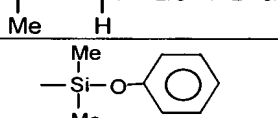

[Table 2]

Polymer	Addition amount of silyl group-containing compound (mmol)	Compound as represented by general formula of Chemical 5 and addition amount thereof (mmol)	Addition amount of triethyl amine (mmol)
H	9.0	 (45)	45
I	9.0	 (45)	45
J	9.0	 (45)	45
K	9.0	 (45)	45
M	9.0	 (45)	45

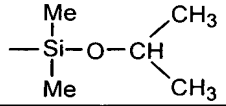
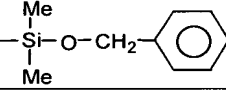
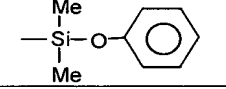
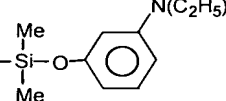
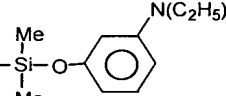
The thus-obtained copolymers are denoted as polymers A to G, J and K and, then, respective propylene contents, iodine values, Mooney viscosities, silyl monomer contents are shown in Tables 3 and 4. Further, in same polymerization conditions as described above, 9.0 mmol of 2-(5-norbornenyl)ethyl dimethyl chlorosilane was added and, after 30 minutes have elapsed, isopropyl alcohol and benzyl alcohol were added, to thereby terminate the polymerization and, then, the resultant samples were denoted as polymers H and I. Still further, in the same polymerization conditions, without adding the silyl group-containing monomer, after 30 minutes have elapsed, methanol was added, to thereby terminate the polymerization and, then, the resultant sample was denoted as polymer L.



[Table 3]

Polymer	Silyl group	Content of propylene (% by weight)	Iodine value	Mooney viscosity	Content of silyl group-containing compound (% by weight)
A	 <chem>C[Si](C)(Oc1ccc(N(CC)CC)cc1)C</chem>	42	15	66	2.2
B	 <chem>C[Si](C)(Oc1cccc(N(CC)CC)c1)C</chem>	44	14	66	1.1
C	 <chem>C[Si](C)(Oc1ccc(N(CC)CC)cc1)C</chem>	44	15	63	6.9
D	 <chem>C[Si](C)(Oc1ccc(N(CC)CC)cc1)C</chem>	43	14	64	2.1
E	 <chem>C[Si](C)(Oc1ccc(CN(CC)CC)cc1)C</chem>	42	16	65	2.2
F	 <chem>C[Si](C)(Oc1ccc(CN(CC)CC)cc1)C</chem>	43	15	64	2.3
G	 <chem>C[Si](C)(Oc1ccccc1)C</chem>	42	16	64	2.3

[Table 4]

Polymer	Silyl group	Content of propylene (% by weight)	Iodine value	Mooney viscosity	Content of silyl group-containing compound (% by weight)
H		43	14	70	2.0
I		41	16	69	2.1
J		43	15	63	2.0
K		42	14	63	1.9
L	none	43	15	65	0
M		19 <sup>1)</sup>	15	21	1.9

<sup>1)</sup> Content of 1-butene.

[0017]

## [Preparation Example 2]

3 liter of purified n-heptane was filled in a separable flask of 5-liter capacity which has previously been substituted by a nitrogen gas and, then, a mixed gas of ethylene, 1-butene and hydrogen with a mixing ratio of 8:1:2 (in mol ratio) was dissolved therein at room temperature in advance. Next, 2-(5-norbornenyl)ethyl dimethyl chlorosilane was added thereto in an amount as shown in Table 2. Further,  $\text{AlEt}_{1.5}\text{Cl}_{1.5}$  and ethyl aluminum dichloride ( $\text{AlEtCl}_2$ ) were added thereto in amounts of 10 mmol and 5 mmol, respectively. Subsequently, 1.5 mmol of a reaction product between  $\text{VOCl}_3$  and ethyl alcohol (1:1 in mol ratio) was loaded thereto while 6.0 ml of ethylidene norbornene was gradually added by using a feed pump, to thereby

initiate a polymerization reaction. The polymerization reaction was performed at 40°C, while the mixed gas of ethylene, 1-butene and hydrogen was continuously fed in a vapor phase and stirred during the polymerization reaction. After 30 minutes have elapsed, a compound as represented by the general formula of Chemical 5 as shown in Table 2 was added. After 10 minutes have elapsed, triethyl amine was added thereto in an amount as shown in Table 2 and, then, further stirred for 20 minutes. Next, 10 ml of dehydrated methanol was added thereto. The resultant copolymer solution was added with a large amount of methanol to be agglomerated. The resultant copolymer was dried by using a hot roll. The thus-dried copolymer was denoted as polymer M. A content of 1-butene, an iodine value, a Mooney viscosity and a content of silyl monomer thereof are shown in Table 4.

[0018]

[Examples 1 to 14]

Polymers A, B, D to G, and J to M as shown in Preparation Example were kneaded in accordance with blending prescription as shown in Table 5 and, then, vulcanized for 20 minutes at 160°C. The results of physical properties are shown in Table 6.

[Table 5]

Polymer	As stated separately
Silica <sup>*1</sup>	As stated separately
Titanium oxide	As stated separately
Process oil <sup>*2</sup>	15
Stearic acid	1
Zinc oxide	5
Diethylene glycol	1
Accelerator M <sup>*3</sup>	0.5
Accelerator T <sub>3</sub> <sup>*4</sup>	1.5
Sulfur	1.5

\*1 Nipsil VN3 (trade name) manufactured by Nippon Silica Industrial Co., Ltd.; specific surface area: 240 m<sup>2</sup>/g

\*2 Paraffin type oil

\*3 Mercaptobenzothiazole

\*4 Tetramethylthiuram monosulfide

[Table 6]

	Polymer (part)	Silica (part)	Titanium oxide (part)	Modulus at 100% elongation (Kgf/cm <sup>2</sup> )	Tensile strength (Kgf/cm <sup>2</sup> )	Elongation (%)
Example 1	A(100)	50	0	24	157	350
Example 2	A(100)	40	10	23	155	360
Example 3	A(100)	40 <sup>*1</sup>	10	22	152	380
Example 4	A(100)	40 <sup>*2</sup>	10	21	155	350
Example 5	B(100)	40	10	19	130	550
Example 6	D(100)	40	10	22	148	370
Example 7	E(100)	40	10	23	151	340
Example 8	F(100)	40	10	20	141	430
Example 9	G(100)	40	10	24	147	320
Example 10	A(80) L(20)	40	10	21	142	420
Example 11	J(100)	40	10	23	145	330
Example 12	K(100)	40	10	24	153	350
Example 13	A(100)	80	10	20	130	400
Example 14	M(100)	40	10	34	173	700

\*1 Reolosil QS 102 (trade name); manufactured by Tokuyama Soda Co., Ltd.; specific surface area: 200 m<sup>2</sup>/g

\*2 Reolosil QS 30 (trade name); manufactured by Tokuyama Soda Co., Ltd.; specific surface area: 300 m<sup>2</sup>/g

[0019]

[Comparative Examples 1 to 9]

Polymers A, C, H, I and L as shown in Preparation Example were kneaded in accordance with blending prescription as shown in Table 5 and, then, vulcanized for 20 minutes at 160°C. The results of physical properties are shown in Table 7.

[Table 7]

	Polymer (part)	Silica (part)	Titanium oxide (part)	Modulus at 100% elongation (Kgf/cm <sup>2</sup> )	Tensile strength (Kgf/cm <sup>2</sup> )	Elongation (%)
Comparative Example 1	L(100)	40	10	16	110	800
Comparative Example 2	C(100)	40	10	30	138	260
Comparative Example 3	A(100)	10	10	18	85	500
Comparative Example 4	A(15) L(85)	40	10	18	120	640
Comparative Example 5	A(100)	40 <sup>*1</sup>	10	19	125	550
Comparative Example 6	A(100)	40 <sup>*2</sup>	10	20	143	460
Comparative Example 7	A(100)	40 <sup>*3</sup>	10	21	148	360
Comparative Example 8	H(100)	40	10	18	127	470
Comparative Example 9	I(100)	40	10	17	124	450

\*1 Carplex #80 (trade name); manufactured by Shionogi & Co., Ltd.; specific surface area: 90 m<sup>2</sup>/g

\*2 Reolosil QS 13 (trade name); manufactured by Tokuyama Soda Co., Ltd.; specific surface area: 130 m<sup>2</sup>/g

\*3 Reolosil QS 38 (trade name); manufactured by Tokuyama Soda Co., Ltd.; specific surface area: 380 m<sup>2</sup>/g

[0020]

[Examples 15 to 17]

Polymer G as shown in Preparation Example was kneaded

in accordance with blending prescription as shown in Table 5 and, then, vulcanized for 20 minutes at 160°C. The coloring property of the copolymer was determined in accordance with the degree of whiteness. As the degree of whiteness becomes larger, the copolymer becomes more favorable in the coloring property. The Tensile properties and the degrees of whiteness of vulcanizates are shown in Table 8.

[Table 8]

	Polymer (part)	Silica (part)	Titanium oxide (part)	Modulus at 100% elongation (Kgf/cm <sup>2</sup> )	Tensile strength (Kgf/cm <sup>2</sup> )	Elongation (%)	Degree of whiteness (%)
Example 15	G(100)	40	5	24	148	330	39
Example 16	G(100)	40	10	24	147	320	50
Example 17	G(100)	40	30	23	130	275	51

[0021]

[Effect of the Invention]

As described above, the ethylene type copolymer rubber composition according to the present invention has an excellent tensile property and is excellent in a coloring property compared with a conventional olefin type copolymer blended with a silica type filler. Therefore, the olefin type copolymer rubber composition according to the invention can be utilized widely and effectively, for example, in exterior articles for automobiles and hoses.

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[Amendment]

[Filing Date] July 26, Heisei 3 (1991)

[Amendment 1]

[Document to be Amended] Specification

[Item to be Amended] Claim

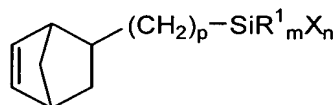
[Method of Amendment] Alteration

[Contents of the Amendment]

[Claims]

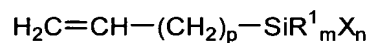
[Claim 1] An olefin type copolymer rubber composition, wherein (A) 100 parts by weight of a rubber component containing at least 20% by weight of a silyl group-containing olefin type copolymer, in which a content of a bonded silyl group-containing unsaturated compound is 0.5 to 5.0% by weight, which is obtained by firstly copolymerizing (a) at least two types of olefin type monomers, (b) a non-conjugated diene and (c) a silyl group-containing unsaturated compound represented by the following general formula:

[Chemical 1]



(I)

and/or



(II)

wherein  $\text{R}^1$  represents a hydrocarbon group having 1 to 20 carbon atoms;

X represents any one halogen of chlorine, bromine and iodine;

p represents an integer of 0 to 5;

q represents an integer of 1 to 20;

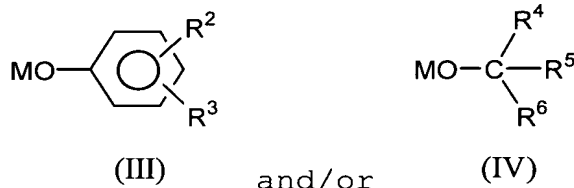
m represents an integer of 0 to 2; and

n represents an integer of 1 to 3, wherein a relation of  $m+n=3$  is established,

in the presence of a catalyst comprising a transition metal compound and an organometallic compound and, then, by allowing the resultant copolymer to react with a compound represented

by the following general formula:

[Chemical 2]



wherein M represents a hydrogen atom or any one alkaline metal of lithium, sodium and potassium;

$R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  each represent the same as the above-described  $R^1$  or any one of a hydrogen atom, a hydrocarbon group having 1 to 20 carbon atoms and containing a tertiary amino group and a tertiary amino group, wherein entire carbon atoms of  $R^4$ ,  $R^5$  and  $R^6$  are 3 or more,

is blended with (B) 20 to 150 parts by weight of a silica type filler having a specific surface area of 160 to 350  $m^2/g$  and (C) 0 to 50 parts by weight of titanium oxide.

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